PB87-129805

Evaluation of an EPA (Environmental Protection Agency) High-Volume Air Sampler for Polychlorinated Dibenzo-P-Dioxins and Polychlorinated Dibenzofurans

Battelle Columbus Div., OH

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Dec 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-129805

EPA/600/4-86/037
December 1986

EVALUATION OF AN EPA HIGH-VOLUME AIR SAMPLER FOR POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

by

F. L. DeRoos, J. E. Tabor, S. E. Miller,
S. C. Watson, and J. A. Hatchel
Battelle Columbus Division
Columbus, Ohio 43201-2693

Contract Number 68-02-4127

Project Officers

Robert G. Lewis and Nancy K. Wilson

Methods Development and Analysis Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/4-86/037	2.
3. RECIPIENT'S ACCESSION NO. PB87 129805/AS	
4. TITLE AND SUBTITLE EVALUATION OF AN EPA HIGH-VOLUME AIR SAMPLER FOR POLY-CHLORINATED DIBENZO-p-DIOXINS AND POLYCHLORINATED DIBENZOFURANS	5. REPORT DATE December 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) F. L. DeRoos, J. E. Tabor, S. E. Miller, S. C. Watson and J. A. Hatchel	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Columbus Division 505 King Avenue Columbus, OH 43201-2693	10. PROGRAM ELEMENT NO. HZW/D109/I1401/1679Y1
	11. CONTRACT/GRANT NO. 68-02-4127
12. SPONSORING AGENCY NAME AND ADDRESS U. S. Environmental Protection Agency Environmental Monitoring Systems Laboratory (RTP) Methods Development & Analysis Division, MDB/AMS Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A High-Volume air sampler was evaluated for collection of poly-chlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). This sampler, which is available from General Metal Works as the Model PS-1 Sampler, consists of a filter, polyurethane foam adsorbent cartridge, air pump, and environmental housing. The use of an alternative adsorbent, silica gel, was also studied. The study was carried out using 1,2,3,4-tetra-chlorodibenzo-p-dioxin, 1,2,4,8-tetrachlorodibenzofuran, 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin 1,2,3,6,7,8-hexachlorodibenzofuran, octachlorodibenzo-p-dioxin, and octachlorodibenzofuran. The overall average retention efficiency for all of the isomers at two concentration levels was 99 percent for both the PUF and the silica gel adsorbents. Silica gel produced lower levels of background interferences than did PUF, but presented some difficulties in cleanup and handling. The desorption efficiency of the PCDD/PCDF isomers from spiked filters was evaluated to assess the extent of migration of these compounds from the filter to the adsorbent. Migration was dependent upon the isomers' chlorination level with the less chlorinated, more volatile isomers generally desorbing more efficiently. Tetrachlorinated isomers desorbed almost completely from the filter and were collected on the adsorbent, whereas the octachlorinated isomers were retained on the filters. Hexachlorinated isomers gave intermediate values of desorption from the filters.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 36
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The acquisition of the information in this document has been funded by the United States Environmental Protection Agency under Contract 68-02-4127 to Battelle Columbus Division. It has been subjected to the Agency's peer review and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that affect health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for assessment of environmental monitoring technology and systems, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing significance to EPA. The evaluation of air sampling methodology for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans provides important information that can be applied to the measurement of the extent of potential human exposure to these compounds.

John C. Puzak
Acting Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ABSTRACT

An EPA High-Volume air sampler was evaluated for retention and migration of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) within the sampler. This sampler, which is available from General Metal Works as the Model PS-1 Sampler, consists of a filter, polyurethane foam adsorbent cartridge, air pump, and environmental housing. The use of an alternative adsorbent, silica gel, was also studied. Because of the high toxicity of selected PCDD/PCDF isomers and the limited availability of pure isomers, the study was carried out using 1,2,3,4-tetrachlorodibenzo-p-dioxin, 1,2,4,8-tetrachlorodibenzofuran, 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin, 1,2,3,6,7,8-hexachlorodibenzofuran, octachlorodibenzo-p-dioxin, and octachlorodibenzofuran.

The sampler retained the isomers with approximately equal efficiencies when either PUF or silica gel was used as the adsorbent. The median retention efficiencies for the PCDD/PCDF isomers ranged from 67 to 124 percent when PUF was used, and from 47 to 133 percent when silica gel was used. In general, the lowest retention efficiencies were observed for the PCDF isomers and the highest retention efficiencies for the PCDDs. The overall average retention efficiency for all of the isomers at two concentration levels was 99 percent for both the PUF and the silica gel adsorbents.

Silica gel produced lower levels of background interferences than did PUF. The detection limits were therefore approximately four times lower for the tetrachlorinated isomers and ten times lower for the hexachlorinated isomers when silica gel was used as the adsorbent. The difference in detection limit was approximately a factor of two for the octachlorinated isomers, which are of higher molecular weight than are the tetrachloro isomer, and consequently are less susceptible to interference.

The desorption efficiency of the PCDD/PCDF isomers from spiked filters was evaluated to assess the extent of migration of these compounds from the filter to the adsorbent. Migration was dependent upon the isomers' chlorination level with the less chlorinated, more volatile isomers generally desorbing more efficiently. Tetrachlorinated isomers desorbed almost completely from the filter and were collected on the adsorbent, whereas the octachlorinated isomers were retained on the filters. Hexachlorinated isomers gave intermediate values of desorption from the filters.

This report was submitted in addition to work previously completed in fulfillment of Contract 68-02-4127 by Battelle Columbus Division under the sponsorship of the U.S. Environmental Protection Agency. This report consolidates two preliminary reports previously submitted describing work carried out during the period of June 1, 1985 to April 30, 1986.

CONTENTS

	Page
Foreword	iii
Abstract	iv
Figures	vii
Tables	vii
1. Introduction	1
2. Conclusions	2
3. Recommendations	4
4. Experimental Procedures	5
Flow rate study	5
Retention study	6
Materials	10
Preparation of standard solutions	10
PUF cartridge cleanup	10
Silica gel cartridge cleanup	11
Extract cleanup	11
HRGC/HRMS analyses	13
5. Results and Discussion	19
Flow rate study	19
Retention study	19
References	27

FIGURES

Number		Page
1	Setup for desorption experiments	7
2	Multilayered silica column	12
3	Chromatogram obtained with high resolution capillary column coupled directly to mass spectrometer	14

TABLES

1	Summary of flow rate experiments	5
2a	Summary of retention experiments (PUF)	8
2b	Summary of retention experiments (silica gel)	9
3	HRGC/HRMS operating parameters	16
4	Exact masses and MID acquisition dwell times	17
5	Flow rates for silica gel adsorbent	19
6	Retention of test compounds spiked into PS-1 Samplers using PUF as the adsorbent	20
7	Retention of test compounds spiked into PS-1 Samplers using silica gel as the adsorbent	22
8	Retention efficiency performance of the PS-1 Sampler for PCDFs and PCDDs using PUF as the adsorbent	25
9	Retention efficiency performance of the PS-1 Sampler for PCDFs and PCDDs using silica gel as the adsorbent	26

SECTION 1

INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are classes of tricyclic compounds that are extremely toxic and are of major environmental concern. Certain isomers, including 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), have LD_{50} values in the parts-per-trillion range for some animal species (1). Major sources of these compounds have been commercial processes involving polychlorinated phenols and polychlorinated biphenyls (PCB). Recently, however, combustion has been shown to be a source of PCDD and PCDF (2). A particularly significant source of these compounds is burning transformers and/or capacitors that contain PCBs and chlorobenzenes.

The objectives of this project were to determine the retention efficiency of the EPA High-Volume air sampler (3) by measuring the retention and migration of selected PCDD and PCDF isomers within the sampler and to evaluate the utility of using silica gel as the adsorbent. Previous studies involving the collection of pesticides, PCBs, semivolatile industrial organic compounds, 1,2,3,4-TCDD and octachlorodibenzofuran (OCDF) (4,5,6,7) had been successful. However, it was anticipated that silica gel would provide a lower background interference level and thus allow lower detection limits to be achieved.

The study consisted of spiking the filters or adsorbent cartridges of EPA High-Volume air samplers with selected PCDD/PCDF isomers. The PCDD/PCDF levels that remained on the filter or the adsorbent cartridge were then measured after a volume of approximately 325 m^3 of air had been pulled through each sampler.

SECTION 2

CONCLUSIONS

The retention efficiencies for the PCDD/PCDF isomers spiked into the samplers were in general quantitative agreement within experimental accuracy. The median retention efficiencies ranged from 67 to 124 percent when PUF was used as the adsorbent and from 47 to 133 percent when silica gel was used. The lowest retention efficiencies were observed for the PCDF isomers, particularly the tetrachlorinated and the hexachlorinated isomers.

Silica gel was found to be suitable as a replacement adsorbent for PUF. It can be packed into the same cartridge as the PUF and produces minimal restriction to the air flow. It does not degrade like PUF, and therefore produces lower levels of interfering compounds. Thus, the detection limits for the PCDD/PCDF were between two and ten times lower when silica gel was used as the adsorbent than when PUF was used.

When the PCDD/PCDF isomers were spiked onto the filter and approximately 325 m^3 of clean air was drawn through the samples, the isomers desorbed and were collected on the adsorbent. The degree of desorption was dependent upon the volatility of the isomer and tended to follow the level of chlorination. The tetrachlorinated isomers were almost completely desorbed from the filter, while the octachlorinated isomers showed only minimal migration. The hexachlorinated isomers desorbed at a degree intermediate to the tetrachlorinated and octachlorinated isomers.

The EPA High-Volume air sampler should be a suitable sampler for collection of PCDD/PCDF isomers from ambient air when either PUF or silica gel is used as the adsorbent. When PUF was used in these studies, the analytical detection limit was approximately 0.2 ng for TCDD and TCDF, which would compare to a theoretical ambient air detection limit of about 0.6 pg/m^3 for a 24-hour sample. The use of chromatographic-grade silica gel improved

detection limits by a factor of nearly four, to about 0.15 pg/m^3. The silica gel, however, was less convenient to work with and required more steps for cleanup.

Due to the desorption of PCDD/PCDF isomers from the filter, the sampler will not provide samples that can be used to determine the particulate matter/vapor concentration distribution of the PCDD/PCDF isomers. If the lowest possible detection limits are needed, silica gel should be used as the adsorbent since it is more stable than PUF and will, therefore, minimize interferences and provide the lowest possible detection limits.

SECTION 3

RECOMMENDATIONS

Because the retention efficiencies observed for 1,2,3,6,7,8-hexachlorodibenzofuran (HxCDF) covered a wide range, additional work is recommended to determine if the measured retentions are realistic or if they resulted from unreliable analytical methodology. This additional work should include the use of an isotopically labelled HxCDF isomer as an internal standard to correct for sample workup losses. It should also include the evaluation of the retention efficiencies of several HxCDF isomers so that variations due to volatility, if significant, could be observed.

Additional work should also be carried out to evaluate further the desorption of PCDD/PCDF isomers from particulate matter. The influence of parameters such as the time between spiking and sampling, the spiking level, and surface characteristics of the particulate matter should be investigated.

SECTION 4

EXPERIMENTAL PROCEDURES

FLOW RATE STUDY

The air flow rates through various bed heights of silica gel were measured to determine if sufficient flow could be achieved. The silica gel was packed into glass cartridges and was held in place using a copper screen and thin layers of glass wool. The cartridge containing the silica gel was placed into a standard High-Volume sampler and flow was established. The experimental setup consisted of a High-Volume Sampler air pump, a dry gas meter, an EPA gas flow calibrator, a filter holder, and a test cartridge containing the silica gel. The system was allowed to equilibrate for 30 minutes prior to recording the dry gas meter readings. The weights, bed heights, and mesh ranges of silica gel that were evaluated are summarized in Table 1.

TABLE 1. SUMMARY OF FLOW RATE EXPERIMENTS

Experiment	Mesh	Weight (g)	Bed Height (cm)
1	35-70	30	2.5
2	35-70	60	4.5
3	6-12	30	1.9
4	6-12	60	3.2
5	6-12	90	5.1
6	6-12	120	6.4
7	6-12	150	7.6

RETENTION STUDY

This evaluation consisted of spiking known levels of PCDD/PCDF isomer into the sampler and measuring the levels of the PCDD/PCDF isomers remaining on the adsorbent cartridges and glass fiber filters following the sampling of approximately 325 m^3 of clean air. Two PCDD/PCDF levels, 150 ng and 5 ng of each isomer, were evaluated in triplicate. The PCDD/PCDF isomers were spiked into the sampler as n-decane solutions. For the experiment in which the spike was placed on the adsorbent cartridge, only the cartridge was analyzed. When the spike was placed on the filter, the filter and cartridge were analyzed separately. Two additional spiked cartridges, one each at the low and high levels, were also prepared for each adsorbent and held in the laboratory during the sampling sessions. Air was not pulled through these cartridges. These were used as reference samples to indicate if irreversible adsorption occurred as a function of time.

The test setup, shown in Figure 1, consisted of two high-volume sampler heads connected in series. The first sampler contained a microfiber glass filter and activated carbon to purify the air going into the second sampler, which contained the test filter and adsorbent cartridge. The retention experiments are summarized in Table 2.

Following the sampling, each of the cartridges and filters was spiked with 2,3,7,8-TCDD-$^{13}C_{12}$ and octachlorodibenzo-p-dioxin-$^{13}C_{12}$ (OCDD-$^{13}C_{12}$) and Soxhlet-extracted with benzene for 18 hours. The high level samples, e.g. those spiked with 150 ng of the native isomers, were spiked with 50 ng of the labelled internal standards, while the low level samples were spiked with 5 ng of each internal standard. The benzene extracts were concentrated using a 3-stage Snyder column, diluted 1:1 with hexane, and cleaned up using acid/base-treated silica and alumina column chromatography. The final solutions were analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The spiking solutions were used to prepare response factor standards, thus eliminating the spiking solution concentration as a variable in the retention efficiency calculations.

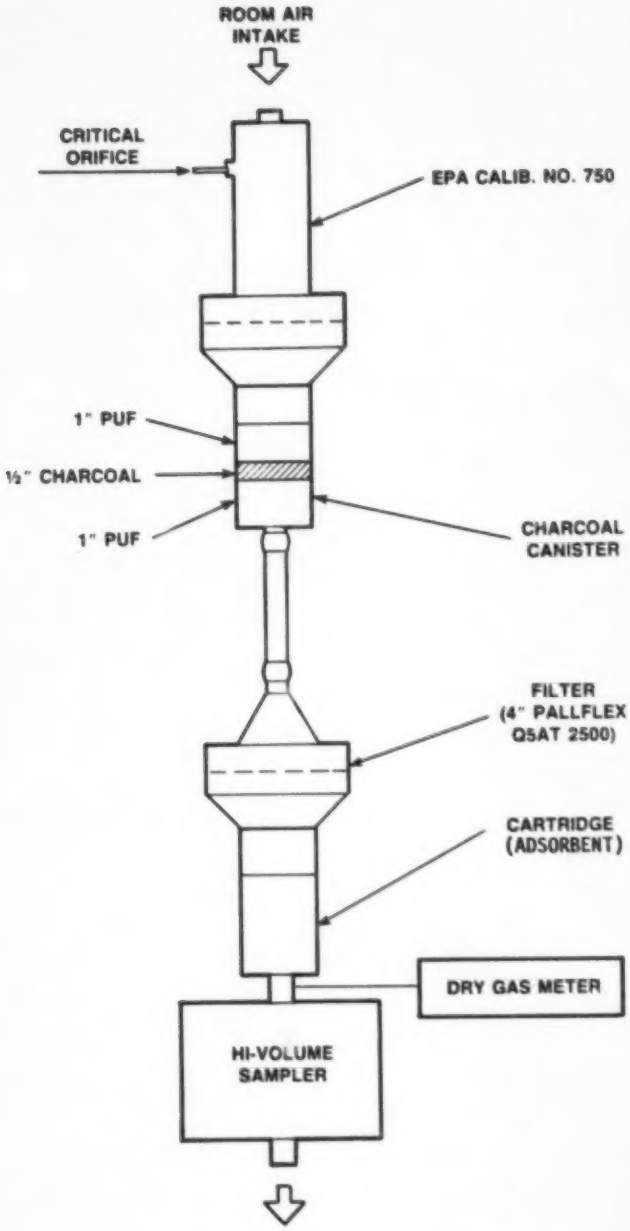


FIGURE 1. SETUP FOR DESORPTION EXPERIMENTS

TABLE 2a. SUMMARY OF RETENTION EXPERIMENTS (PUF)

Experiment Number	Test Description	Spike Quantity, ng
1	PUF High Level Spike	150
2	PUF High Level Spike	150
3	PUF High Level Spike	150
4	Lab Blank	--
5	Filter High Level Spike	150
6	Filter High Level Spike	150
7	Filter High Level Spike	150
8	Lab Blank	--
9	PUF High Level Spike (held)	150
10	PUF Low Level Spike	5
11	PUF Low Level Spike	5
12	PUF Low Level Spike	5
13	Lab Blank	--
14	Filter Low Level Spike	5
15	Filter Low Level Spike	5
16	Filter Low Level Spike	5
17	Lab Blank	--
18	PUF Low Level Spike (held)	5
19	PUF Blank	--

TABLE 2b. SUMMARY OF RETENTION EXPERIMENTS (SILICA GEL)

Experiment Number	Test Description	Spike Quantity, ng
1	Silica Gel High-Level Spike	150
2	Silica Gel High-Level Spike	150
3	Silica Gel High-Level Spike	150
4	Lab Blank	--
5	Filter High-Level Spike	150
6	Filter High-Level Spike	150
7	Filter High-Level Spike	150
8	Lab Blank	--
9	Silica Gel High Level Spike (held)	150
10	Silica Gel Low-Level Spike	5
11	Silica Gel Low-Level Spike	5
12	Silica Gel Low-Level Spike	5
13	Lab Blank	--
14	Filter Low-Level Spike	5
15	Filter Low-Level Spike	5
16	Filter Low-Level Spike	5
17	Lab Blank	--
18	Silica Gel Low-Level Spike (held)	5
19	Silica Gel Blank	--

Materials

The solvents used for sample workup and for cleaning the adsorbents were Distilled-in-Glass grade purchased from Burdick and Jackson Laboratories, Muskegum, MI. The 35-70 and 6-12 mesh silica gel was purchased from Aldrich Chemical Company (21,439-6) and the alumina from BioRad, Richmond, CA. The native and isotopically labelled PCDD/PCDF isomers were obtained from Cambridge Isotopes, Cambridge, MA. The n-decane used to prepare the native and isotopically labelled standard solutions was obtained from Aldrich Chemicals, Milwaukee, WI as Gold Label grade (D90-1).

Preparation of Standard Solutions

The native PCDD/PCDF isomers were obtained as neat materials, while the isotopically labelled isomers were obtained as isooctane solutions. The native PCDD/PCDF standard solutions were prepared gravimetrically and were used as the primary standards. The isotopically labelled solutions used as internal standards were prepared as dilutions of the stock solutions obtained from Cambridge Isotopes. All spiking solutions were stored in a freezer at approximately -15°C except when being used.

The native spiking solutions were prepared at concentrations of 50 pg/µl and 600 pg/µl for the low level and high level spikes, respectively. These concentrations required spiking volumes of 100 µl and 250 µl to achieve the 5 ng and 150 ng spiking levels. The isotopically labelled internal standards were prepared at concentrations of 50 pg/µl and 250 pg/µl.

PUF Cartridge Cleanup

The PUF cartridges were extracted with solvent before use in the experiments. A modification of the cleanup described by Thrane and Mikelsen (6) was used. Cartridges were rinsed sequentially with toluene, acetone, and diethyl ether/hexane (5:95, v/v) by placing them in 3-L beakers and compressing them with the base of a 1-L graduated cylinder. After the last rinse they were compressed to force out as much solvent as possible and then placed into the glass cartridge holders (2.3 in. I.D., 5 in. length). The cartridge assemblies were placed in Soxhlet extractors and extracted with benzene. After approximately 24 hours, they were removed from the extractors,

drained, and placed in a vacuum oven. The oven was evacuated to approximately 250 torr, flushed twice with dry nitrogen gas and held evacuated at 25°C overnight. The PUF cartridge assemblies were stored in screw-cap wide mouth jars, which were wrapped with aluminum foil to protect them from light.

Silica Gel Cartridge Cleanup

Silica gel (chromatographic-grade silicic acid, 35-70 mesh, No. 24, 217-9, Aldrich Chemical, Milwaukee, WI) was activated by heating in a Pyrex glass tube furnace under purified nitrogen gas purge at a temperature of 180°C for one hour. The glass tube was then removed from the furnace and cooled to ambient temperature while the nitrogen gas flow was maintained. Nitrogen flow was discontinued, and the silica gel was washed consecutively with 350 mL aliquots of methanol and methylene chloride. The methylene chloride-saturated adsorbent was returned to the furnace and heated to 50°C with nitrogen gas purge. After 20 minutes, the temperature was raised gradually to 180°C and maintained for 90 minutes. The dry silica gel was cooled to ambient temperature and transferred to a fritted glass extraction thimble. It was Soxhlet-extracted for 12 hours with methylene chloride, dried under nitrogen gas and heated to 180°C for 1 hour. The silica gel was then cooled and transferred to sampler cartridges. Each cartridge was loaded with approximately 60 g of silica gel, which was held in the sampler by plugs of glass wool. The silica gel bed height was approximately 4.5 cm. This quantity of silica gel was the maximum that would allow sufficient air flow for sampling. The cartridges were placed into a Soxhlet extractor and extracted for 18 hours using benzene. They were then removed from the Soxhlet apparatus, placed in an oven and maintained at 120°C until they were used.

Extract Cleanup

Column chromatography was employed both to isolate the PCDD and PCDF isomers and to minimize coextracted interferences in the extracts (8,9,10). The process consisted of eluting the extract through two adsorption columns. The first column, illustrated in Figure 2, contained alternate layers of activated silica gel, 44 percent concentrated sulfuric acid on silica gel,

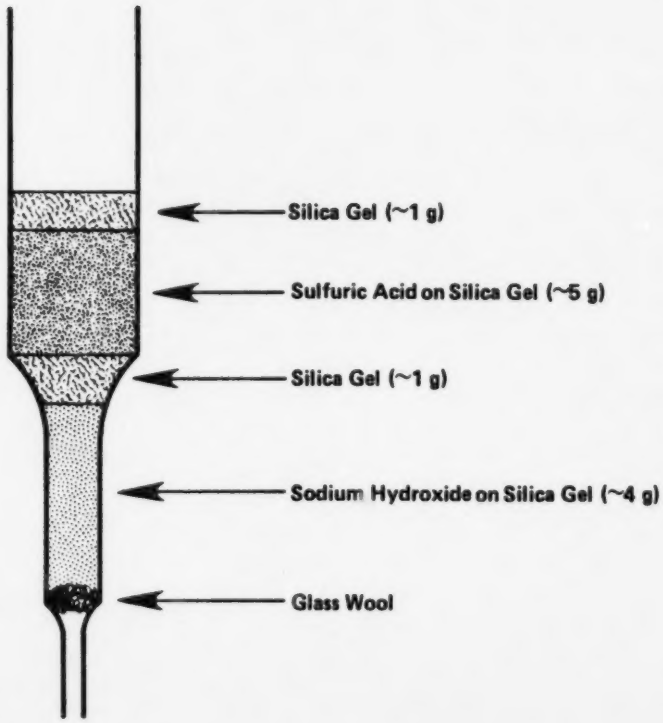


FIGURE 2. MULTILAYERED SILICA COLUMN

silica gel, and 33 percent 1 M sodium hydroxide on silica gel. This column was eluted with 70 mL of hexane.

The eluate from the multilayered silica column was collected, concentrated to near dryness using a gentle stream of nitrogen gas and redissolved in 1 mL of hexane. The hexane solution was then added to the top of a column containing 2 g of basic alumina, which had been activated at 300°C for 90 minutes. This column was eluted with 15 mL of hexane, 5 mL of dichloromethane/hexane (3:97, v/v) and 20 mL of hexane/dichloromethane (1:1, v/v) in sequence.

The hexane/dichloromethane (1:1, v/v) eluate contained the PCDD and PCDF isomers. It was collected in a 18 mL concentrator tube and concentrated to near dryness at 30°C with a gentle stream of ultrapure nitrogen gas. During the concentration step, the sides of the tube were rinsed with 1 mL of dichloromethane. The dichloromethane was allowed to evaporate to dryness (on standing) without the use of the nitrogen gas stream. The residue was dissolved in 20 µL of n-decane containing 10 ng of 1,2,3,4,-TCDD-$^{13}C_{12}$ which was used to calculate the absolute recoveries of the internal standards. The extract was stored at 0°C and protected from light until it was analyzed.

HRGC/HRMS Analyses

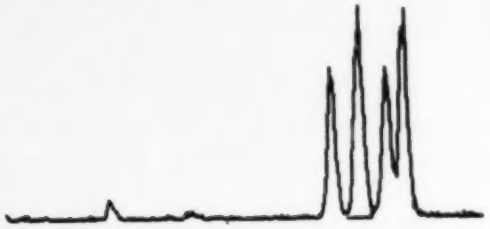
The extracts were analyzed and the PCDD and PCDF were detected and quantified with combined capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS) (10). The HRGC/HRMS consisted of a Carlo Erba Model 4160 gas chromatograph interfaced directly into the ion source of a VG Model 7070H mass spectrometer. Although zero dead volume couplers and efficient transfer lines are available, they still degrade chromatographic resolution because of analyte adsorption. The use of a direct-coupled capillary column, used in this study, can be utilized to minimize the loss of resolution. An example of the chromatographic resolution obtained by direct interface of the capillary column to the mass spectrometer ion source is shown in Figure 3.

The mass spectrometer was operated in the electron impact (EI) ionization mode at a mass resolution of 10,000-12,000 (M/ΔM, 10 percent valley definition). This mass resolution is sufficient to resolve the test compounds from most potential interferences. The operating parameters of the HRGC/HRMS

SIR REPORT. FILE - 348318 .SD RUN - 1 HRMID 2,3,7,8-TCDD + C13

UNCALIBRATED.

MASS	RETENTION TIME	HEIGHT	AREA	CONC.(H)
320	0 HRS 18 MINS 58 SECS	106.9140	545.8865	0.0000



322	0 HRS 18 MINS 58 SECS	114.8820	662.7330	0.0000

332	0 HRS 18 MINS 56 SECS	73.5078	378.8467	0.0000

334	0 HRS 18 MINS 56 SECS	84.7266	442.3453	0.0000

FIGURE 3. HIGH RESOLUTION CAPILLARY COLUMN CHROMATOGRAM

are summarized in Table 3. The data were acquired by multiple ion detection (MID), with two molecular ion masses from each of the analytes and two from each internal standard being monitored. The masses were selected and the data were acquired using a VG Model 2035 Data System. The exact masses and acquisition dwell times are listed in Table 4. A perfluorokerosene (PFK) mass was monitored during the analyses to calibrate the MID masses and to provide correction for mass drift. Although the short-term stability of modern mass spectrometers is typically better than 10 ppm, long-term stability during an HRGC/HRMS analysis (20-30 minutes) may be as poor as 50 ppm without the use of a lock mass.

Quantification

The PCDF/PCDD isomers were quantified by comparing the sum of the two ions monitored for each congener class to the sum of the two ions monitored for the corresponding internal standard. The 2,3,7,8-TCDD-$^{13}C_{12}$ was used to quantify the TCDD and hexachloro isomers and the OCDD-$^{13}C_{12}$ used for the octachloro isomers. Experimental relative response factors were calculated from daily analyses of a test mixture prepared from the spiking solutions. These response factors were included in all calculations used to quantify the data. The response factors were calculated using the sum of the two ions monitored for each class of isomers compared to the sum of the two ions monitored for the corresponding internal standard. The average experimental response factors were:

Analyte	Silica Gel Study	PUF Study
TCDF	--	1.788
TCDD	1.00	0.938
HxCDF	0.506	1.727
HxCDD	0.583	2.388
OCDF	1.14	0.986
OCDD	1.17	1.052

The formula used for quantifying the isomers was:

$$\text{Quantity/sample} = \frac{\text{Areas of Quantification Masses X Quantity of Int. Std.}}{\text{Area of Internal Standard Masses X Res. Factor}}$$

TABLE 3. HRGC/HRMS OPERATING PARAMETERS

Mass Resolution	10,000-12,000 (M/ΔM, 10% valley definition)
Electron Energy	70 eV
Accelerating Voltage	4,000 volts
Source Temperature	200°C
Preamplifier Gain	10^7 volts/amp
Electron Multiplier Gain	-10^6
Transfer Line Temperature	280°C
Capillary Column	30 m DB-5 Fused Silica
Injector Temperature	300°C
Column Temp - Initial	160°C
Column Temp - Final	290°C
Carrier Gas	Helium
Flow Velocity	30 cm/sec
Injection Mode	Splitless
Injection Volume	2 µL

TABLE 4. EXACT MASSES AND MID ACQUISITION DWELL TIMES

Mass	Dwell Time, ms	Description
303.9016	45	Native TCDF
305.8987	45	Native TCDF
315.9418	45	TCDF-$^{C}13_{12}$
317.9389	45	TCDF-$^{C}13_{12}$
319.8965	45	Native TCDD
321.8936	45	Native TCDD
331.9368	45	TCDD-$^{C}13_{12}$
333.9338	45	TCDD-$^{C}13_{12}$
373.8207	45	Native HxCDF
375.8178	45	Native HxCDF
380.9761	45	PFK Lock Mass
389.8156	45	Native HxCDD
391.8127	45	Native HxCDD
441.7428	45	Native OCDF
443.7398	45	Native OCDF
457.7377	45	Native OCDD
459.7347	45	Native OCDD
469.7779	45	OCDD-$^{C}13_{12}$
471.7749	45	OCDD-$^{C}13_{12}$

A limit of detection for each of the isomers was calculated from the laboratory method blank analyses. The formula used to calculate the limit of detection was:

Limit of Detection/sample =

$$\frac{\text{Heights of Quantification Masses X Quantity of Internal Standard X 2.5}}{\text{Heights of Internal Standard Masses X Res. Factor}}$$

Quality Assurance

The operation of the HRGC/HRMS was evaluated at least once every 8 hours by analyzing standard mixtures of PCDD/PCDF isomer. These included mixtures of native and isotopically labelled isomers to evaluate the accuracy of quantification, mixtures of selected PCDD/PCDF isomers to evaluate the stability of the chromatographic elution windows, and a mixture of TCDD isomers to evaluate the chromatographic resolution. The mass accuracy of the MID unit was also evaluated at least every 4 hours by focusing selected ion masses from perfluorokerosene (PFK) and correcting the slope to account for minor variations. Mass focus stability was assured by the use of a reference PFK "lock mass" to correct for any mass focus drift. Mass resolution was checked every 4 hours by peak matching selected PFK ion masses. Solvents, silica gel cartridges, and chromatographic adsorbents were periodically analyzed as method blanks to demonstrate freedom from contamination. No indication of contamination was observed in any of the method blanks. Decane was also injected into the HRGC/HRMS to show that the PCDD/PCDF were not carried over to subsequent analyses by contamination of syringes, septa, or the capillary columns.

SECTION 5

RESULTS AND DISCUSSION

FLOW RATE STUDY

Adequate flow air rates for sampling (>150 std. L/min) were achieved for both meshes of silica gel and for all bed heights evaluated. Although the 6-12 mesh silica gel could be used with bed heights of up to 7.6 cm, the finer 35-70 mesh material was chosen to provide the greatest surface area for collection of the test PCDD/PCDF isomers. The results of the flow rate study are summarized in Table 5.

TABLE 5. FLOW RATES FOR SILICA GEL ADSORBENT

Experiment	Weight (g)	Mesh	Bed Height (cm)	Flow Rate (L/min)
1	30	35-70	2.5	190
2	60	35-70	4.5	160
3	30	6-12	1.9	230
4	60	6-12	3.2	220
5	90	6-12	5.1	220
6	120	6-12	6.4	215
7	150	6-12	7.6	215

RETENTION STUDY

The results of the retention experiments are summarized in Tables 6 and 7. Table 6 contains the results from the experiments in which PUF was used as the adsorbent, while Table 7 contains the results from the experiments in which silica gel was used.

TABLE 6. RETENTION OF TEST COMPOUNDS SPIKED INTO PS-1 SAMPLERS WITH PUF AS THE ADSORBENT

Spike Location	Filter/ PUF	Spike Level (ng)	Percent Recovery					
			TCDF	TCDD	HxCDF	HxCDD	OCDF	OCDD
Filter	Filter	150	0.3	1.5	4.2	9.9	56	88
	PUF		73	95	112	114	21	16
	Filter + PUF		73	96	116	124	77	104
Filter	Filter	150	0.3	1.8	4.7	9.2	55	83
	PUF		95	98	94	90	36	14
	Filter + PUF		95	100	99	99	91	97
Filter	Filter	150	0.4	2	5.4	12	59	88
	PUF		78	90	102	89	17	9.8
	Filter + PUF		78	92	107	101	76	98
Median	Filter + PUF	150	78	96	107	101	77	98
Filter	Filter	5	2	0	0	4	21	32
	PUF		90	116	91	101	74	57
	Filter + PUF		92	116	91	105	95	89
Filter	Filter	5	0	0	0	0	29	45
	PUF		76	88	103	110	69	57
	Filter + PUF		76	88	103	110	98	102
Filter	Filter	5	1	0	3	4	27	45
	PUF		72	81	86	100	70	88
	Filter + PUF		73	81	89	104	97	133
Median	Filter + PUF	5	76	88	91	105	97	102

TABLE 6. (Continued)

Spike Location	Spike Level (ng)	Percent Recovery					
		TCDF	TCDD	HxCDF	HxCDD	OCDF	OCDD
PUF Cartridge	150	106	108	102	106	109	106
PUF Cartridge	5	105	106	85	95	105	109
Blank	--	ND	ND	ND	ND	ND	ND
Blank	--	ND	ND	ND	ND	ND	ND
PUF Cartridge	150	31	108	40	90	110	108
PUF Cartridge	150	70	99	79	96	97	100
PUF Cartridge	150	67	104	75	100	107	110
Median	150	67	104	75	96	107	108
PUF Cartridge	5	81	122	120	135	105	97
PUF Cartridge	5	94	112	114	124	120	112
PUF Cartridge	5	96	105	103	117	109	100
Median	5	94	112	114	124	109	100
Blank	--	ND	ND	ND	ND	ND	ND
Blank	--	ND	ND	ND	ND	ND	ND
Blank	--	ND	ND	ND	ND	ND	ND

ND = Not Detected at a detection limit of approximately 0.2 ng for TCDF/TCDD, 0.5 ng for HxCDF/HxCDD and 1.1 ng for OCDF/OCDD.

TABLE 7. RETENTION OF TEST COMPOUNDS SPIKED INTO PS-1 SAMPLERS WITH SILICA GEL AS THE ADSORBENT

Spike Location	Filter/ Silica Gel	Spike Level (ng)	Percent Recovery				
			TCDD	HxCDF	HxCDD	OCDF	OCDD
Filter	Filter	150	3.7	5.8	43	68	96
	Silica Gel		77	65	78	18	2.0
	Filter + Silica Gel		81	71	121	86	98
Filter	Filter	150	4.9	7.8	60	61	99
	Silica Gel		75	49	73	27	3.1
	Filter + Silica Gel		80	57	133	88	102
Filter	Filter	150	4.9	6.6	27	54	88
	Silica Gel		69	73	124	17	2.3
	Filter + Silica Gel		74	80	151	71	90
Median	Filter + Silica Gel	150	80	71	133	86	98
Filter	Filter	5	1.6	7.1	9.4	83	99
	Silica Gel		61	68	120	7.6	6.9
	Filter + Silica Gel		63	75	129	91	106
Filter	Filter	5	1.3	4.1	6.2	76	106
	Silica Gel		88	74	100	7.8	6.7
	Filter + Silica Gel		89	78	106	84	113
Filter	Filter	5	1.8	5.9	7.1	91	127
	Silica Gel		73	46	29	8.8	6.7
	Filter + Silica Gel		75	52	36	100	134
Median	Filter + Silica Gel	5	75	75	106	91	113

TABLE 7 . (Continued)

Spike Location	Filter/ Silica Gel	Spike Level (ng)	Percent Recovery TCDD	HxCDF	HxCDD	OCDF	OCDD
Silica Gel	Silica Gel Spike	150	108	46	129	115	101
Silica Gel	Silica Gel Spike	5	82	38	112	85	95
Blank	--	--	ND	ND	ND	ND	ND
Blank	--	--	ND	ND	ND	ND	ND
Silica Gel	Filter	150	92	4	101	90	104
Silica Gel	Silica Gel	150	89	47	105	97	101
Silica Gel	Filter + Silica Gel	150	89	61	138	99	101
Median	Filter + Silica Gel	150	89	47	105	97	101
Silica Gel	Filter	5	92	38	127	110	118
Silica Gel	Silica Gel	5	81	64	132	99	119
Silica Gel	Filter + Silica Gel	5	92	116	163	108	128
Median	Filter + Silica Gel	5	92	64	132	108	119
Blank	--	--	ND	ND	ND	ND	ND
Blank	--	--	ND	ND	ND	ND	ND
Blank	--	--	ND	ND	ND	ND	ND

ND = Not Detected at a detection limit of approximately 0.05 ng for TCDD and for HxCDF/HxCDD and 0.5 ng for OCDF/OCDD.

The average retention efficiency for the PCDD/PCDF isomers spiked on filters was dependent upon the volatility of the particular isomer. In general, the tetrachlorinated isomers desorbed from the filters and were collected on the adsorbent, while the octachlorinated isomers remained on the filters. The hexachlorinated isomers exhibited intermediate behavior. When the data from the PUF and silica gel experiments are averaged at the two spiking levels, approximately 1.8 percent of the tetrachlorinated isomer spikes was retained on the filters, while 83 percent of the octachlorinated isomer spikes was retained after sampling. The hexachloro isomer spikes were retained on the filters at approximately 10 percent.

The average performance of the sampler for retention of PCDD/PCDF isomers is summarized in Tables 8 and 9. Table 8 summarizes the results for the sampler when PUF is used as the adsorbent and Table 9 the results when silica gel is used. All of the retention efficiencies are within $\pm$25 percent of quantitative, except for the two hexachloro isomers which vary by approximately $\pm$30 percent.

The adsorbent retention efficiencies for the HxCDD and HxCDF isomers were the lowest and the most variable of those measured. Although it is possible that these isomers were breaking through the adsorbents, it is also possible that they were lost during the sample workup. Since an isotopically labelled hexachlorinated dioxin or furan was not available for use as an internal standard, losses due to extraction and cleanup were corrected based on the recovery of the labelled tetrachlorinated standards. It was assumed that the volatility and extraction efficiency of these standards were similar to the hexachlorinated isomers, however, the validity of these assumptions has not been tested for all matrices.

TABLE 8. RETENTION EFFICIENCY PERFORMANCE OF THE PS-1 SAMPLER FOR PCDFs AND PCDDs USING PUF AS THE ADSORBENT

Medium	Spike Level[1], ng/m^3	Average Percent Recovery					
		TCDF	TCDD	HxCDF	HxCDD	OCDF	OCDD
Filter	0.5[1]	0.3[2]	1.5	4.8	10	57	86
PUF		82	95	103	97	25	13
Total Accountability		82	96	108	107	82	99
Filter	0.02	2	0	1	3	26	41
PUF		79	95	93	104	71	67
Total Accountability		81	95	94	107	97	108

[1] Spike levels based on total weight of PCDD/PCDF isomer spiked, assuming 325 m^3 of air were sampled.

[2] Average for three experiments.

TABLE 9. RETENTION EFFICIENCY PERFORMANCE OF THE PS-1 SAMPLER FOR PCDFs AND PCDDs USING SILICA GEL AS THE ADSORBENT

Medium	Spike Level ng/m^3	Average Percent Recovery				
		TCDD	HxCDF	HxCDD	OCDF	OCDD
Filter	0.5	4.5	6.7	43	61	94
Silica Gel		74	62	92	21	2.5
Total Accountability		78	69	140	82	97
Filter	0.02	1.6	5.7	7.6	83	110
Silica Gel		74	63	83	8.1	6.8
Total Accountability		76	68	91	91	120

REFERENCES

1. Polar, A., Kuntson, J., Ann. Rev. Pharmacol. , 22, pp. 517-554 (1982).

2. Lustenhouwer, J.W.A., Olie, K., Hutzinger, O., Chemosphere, 9, pp. 501-522 (1980).

3. Lewis, R. G., and Jackson, M. D., Anal. Chem., 54, 592-594 (1982).

4. Lewis, R. G., Brown, A. R., and Jackson, M. D., Anal. Chem., 49, 1668-1672 (1977).

5. Lewis, R. G., and MacLeod, K. E., Anal. Chem., 54, 310-315 (1982).

6. Thrane, K. E., and Mikalsen, A., "High Volume Sampling of Airborne Polycyclic Aromatic Hydrocarbons Using Glass Fiber Filters and Polyurethane Foam". Atmos. Environ., 15(6), 909-918 (1981).

7. "Evaluation of the EPA High-Volume Sampler for Collection of Polychlorinated Dibenzo-p-dioxins", DeRoos, F. L., Tabor, J. E., Miller, S. E., Watson, S. C., and Hatchel, J. A., Progress Report, EPA Contract 68-02-3487, Battelle Columbus Laboratories, Columbus, Ohio, September 24, 1984.

8. Determination of Tetra-Hexa CDF, Tetra-Penta CDD, and Tetra-Penta Biphenylenes in Air Samples from Floors 3, 5, 7, and 9 of the Binghampton New York State Office Building. Smith, R. M., Hiler, D. O'Keefe, P., and Aldons, K. Report from Laboratory of Organic Analytical Chemistry, New York State Dept. of Health, Albany, NY, June 27, 1983.

9. Determination of 2,3,7,8-TCDD in Soil and Sediment, September 1983, U.S. Environmental Protection Agency, Region VII Laboratory, Kansas City, Kansas.

10. Harless, R. L., Oswald, E. O., Wilkinson, M. K., Dupuy, A. E., Jr., McDaniel, D. D., and Tai, H., "Sample Preparation and Gas Chromatography-Mass Spectrometry. Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin", Anal. Chem., 52, 1239-1245 (1980).